



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification⁴ : C04B 28/02 // (C04B 28/02 C04B 24:06, 24:14, 24:16 C04B 24:26, 24:38)</p>	<p>A1</p>	<p>(11) International Publication Number: WO 86/ 00291</p> <p>(43) International Publication Date: 16 January 1986 (16.01.86)</p>
<p>(21) International Application Number: PCT/EP85/00294</p> <p>(22) International Filing Date: 18 June 1985 (18.06.85)</p> <p>(31) Priority Application Numbers: 59/125353 657,307</p> <p>(32) Priority Dates: 20 June 1984 (20.06.84) 3 October 1984 (03.10.84)</p> <p>(33) Priority Countries: JP US</p> <p>(71) Applicant: SANDOZ AG [CH/CH]; Lichtstrasse 35, CH-4002 Basel (CH).</p> <p>(72) Inventors: KOZAKURA, Teruo ; Nisso Master Builders Apt. B, No. 503, 2722, Hagizono, Chigasaki-shi, Kanagawa-ken (JP). OHTA, Akira ; Nisso Master Builders Apt. B, No. 103, 2722 Hagizono, Chigasaki-shi, Kanagawa-ken (JP). NEMOTO, Tohru ; Nisso Master Builders Apt. B, No. 107, 2722, Hagizono, Chigasaki-shi, Kanagawa-ken (JP). SHIMIZU, Tet-</p>		<p>suij; Nakayama Cho-Midori-ku, Yokohama-shi, Kanagawa-ken (JP). SPROUTS, Sandra, R. ; 7318 Lamson, Oakwood Village, OH 44146 (US). MOORE, Richard, H. ; 10110 Parkview Avenue, Garfield Heights, OH 44125 (US).</p> <p>(81) Designated States: AU, BE (European patent), BR, CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, NO, SE (European patent).</p> <p>Published <i>With international search report. With amended claims.</i></p>
<p>(54) Title: IMPROVEMENTS IN OR RELATING TO ORGANIC COMPOUNDS FOR CEMENT MIXES</p>		
<p>(57) Abstract</p> <p>Aggregate containing cement mixes, such as grouts, mortars, and concrete for use in construction or for cementing brick, cement block, stucco and even ceramic tiles. These mixes comprise: a) hydraulic cement; b) one or more flocculating agents, selected from sodium alginate, water soluble cellulose ether, polyacrylate, polyacrylamide, guar gum, gelatin, chitosan, dextrin and dialdehyde starches; c) one or more water reducing agents selected from sulphonated naphthalene/formaldehyde condensates, sulphonated melamine/formaldehyde condensates, lignosulphonates, modified lignosulphonates, salts of polyhydroxy carboxylic acids, polyhydroxy carboxylic acids, glucosaccharides, copolymers of linear or cyclic C₄₋₆-olefins and unsaturated ethylenic dicarboxylic acids; d) aggregate; and e) water.</p>		

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Improvements in or relating to organic compounds for cement mixes.

The invention relates to aggregate containing cement mixes (such as grouts, mortars and concrete) for use in construction and for cementing brick, cement block, stucco and even ceramic tiles.

According to the invention there is provided a cement mix comprising:

- a) hydraulic cement;
- b) one or more flocculating agents, selected from sodium alginate, water soluble cellulose ether, polyacrylates, polyacrylamides, guar gum, gelatin, chitosan, dextrin and dialdehyde starches;
- c) one or more water reducing agents selected from sulphonated naphthalene/formaldehyde condensates, sulphonated melamine/formaldehyde condensates, lignosulphonates, modified lignosulphonates, salts of polyhydroxy carboxylic acids, polyhydroxy carboxylic acids, glucosaccharides, copolymers of linear or cyclic C₄₋₆-olefins and unsaturated ethylenic dicarboxylic acids;
- d) aggregate; and
- e) water.

Preferred flocculating agents are selected from water soluble ethers, preferably hydroxypropyl-methyl-cellulose and sodium carboxymethyl cellulose, and sodium alginate.

Preferably when the water reducing agent is a copolymer of an unsaturated ethylenic dicarboxylic acid, the acid is itaconic acid.

Preferably when the flocculating agent is a polyacrylate it is sodium polyacrylate.

Preferably when the water reducing agents are polyhydroxy carboxylic acids these are C_{6-8} mono- or di-carboxylic acids, more preferably gluconic or glucoheptonic acids. Preferably the salts of carboxylic acids are those of the preferred and more preferred carboxylic acids. Most preferred carboxylic acid salts are sodium gluconates and sodium glucoheptonates.

Preferred water reducing agents are selected from sulphonated naphthalene/formaldehyde condensates, sulphonated melamine/formaldehyde condensates, sodium or calcium lignosulphonate and alkali-treated or ultra-filtered modified lignosulphonates.

Preferably the amount of flocculating agent present is 0.01 to 0.5 % by weight (based on the dry weight of cement present). The amount of flocculating agent used is preferably dependent on its molecular weight. Where the molecular weight is at the higher end of the range (e.g. a molecular weight of approximately 140,000) the more preferred amount of flocculating agent used is 0.01 to 0.1 %, most preferably 0.03 to 0.1 % (based on the dry weight of cement present). Where the molecular weight is at the lower end of the range (e.g. a molecular weight of approximately 15-20,000) more preferably the amount of flocculating agent used is 0.10 to 0.4 % most preferably 0.1 to 0.3 % (based on the dry weight of cement present).

The amount of water reducing agent varies depending on the efficiency of the water reducing agent and the amount needed to compensate for loss in fluidity properties due to the flocculating agent.

Preferably the amount of water reducing agent present is 0.1 to 2 % , more preferably 0.2 to 1.3 %, most preferably 0.2 to 1.0 % by weight (based on the dry weight of cement present).

- 2A -

Preferably aggregate includes one or more of the following natural silica sand, manufactured or processed sand, blast furnace slag, masonry sand, crushed stone, gravel and any other coarse aggregate.

Preferably the amount of aggregate present is 200 to 800 % by weight (based on the dry weight of cement present). Where the aggregate is fine aggregate the more preferred amount is 200 to

600 % and where the aggregate is fine and coarse aggregate the more preferred range is 400 to 800 %. In concrete generally at least 40 % of the aggregate is fine aggregate.

Preferably the amount of water present is 25 to 65 % by weight (based on the dry weight of cement present). More preferably the amount of water present is 30 to 60 %, most preferably 35 to 55 %.

In cement mixes according to the invention the hydraulic cement preferably comprises 10 to 30 %, more preferably 15 to 25 % of the total weight of cement mix.

Hydraulic cement preferably includes portland cements, blended cements, high alumina cements and pozzolaic cements. Portland cement comprises tricalcium silicate (alite), dicalcium silicate (belite), tricalcium aluminate and tetracalcium alumina ferrite. Further minor components include sodium and potassium oxides and magnesium oxide. Calcium sulphate may also be ground into the cement. Blended cements are those containing cement and finely divided blast-furnace slag and/or fly ash.

The flocculating agent and water reducing agent can be worked simultaneously or singly at any stage into the cement mixture and before or after any other cement admixtures have been added.

Further, according to the invention, there is provided a method for preparing a cement mix including aggregate and water comprising adding to the cement mix one or more

flocculating agents selected from sodium alginate, water soluble cellulose ethers, polyacrylates, polyacrylamides, guar gum, gelatin, chitosan, dextrin and dialdehyde starches and one or more water reducing agents selected from sulphonated naphthalene/formaldehyde condensates, sulphonated melamine/formaldehyde condensates, lignosulphonates, modified lignosulphonates, salts of polyhydroxy carboxylic acids, polyhydroxy carboxylic acids, glucosaccharides, copolymers of linear and cyclic C₄₋₆-

olefins and unsaturated ethylenic dicarboxylic acids.

Loss in fluidity in concrete is measured by slump loss. Slump is a measure of how much a given height of a conical cement specimen will drop from its original height when no longer constrained by the mould of a slump cone. A slump cone is standardized at 30.6 cms. Therefore, a cement mix with a slump of 20 cms means that the mix has settled to about 1/3 of its original height. Slump loss is a measure of how much slump diminishes on standing for a given time.

Loss in fluidity for mortars and grouts may be measured by the known vibration drop table test for spreading loss which is analogous to the slump test.

One advantage of a method according to the invention is that fluid loss can effectively be reduced and fluidity is maintained at roughly the same level for a long period of time. In the case of concrete it has been found that there is practically no slump loss for approximately 1 hour after combined addition of the flocculating agent and the water reducing agent. Further, there is no need to increase the amount of water present to compensate for slump loss as was necessary in the past. (This increase caused the physical properties of the concrete to be impaired). Further, the physical properties of the concrete will be improved by the addition of the water reducing agent and the flocculating agent, for instance the resistance of concrete to segregation will be increased and the rheological characteristics and pumpability will be increased.

In the past there has been a tendency to avoid adding a high molecular flocculating agent to a cement mix, especially concrete, since fluidity would generally be greatly reduced. Further, where a water reducing agent alone has been added although the fluidity of the cement mix is increased immediately after addition, it has rapidly deteriorated.

Still further according to the invention there is provided a mortar comprising:

- a) a hydraulic cement
- b) a water soluble cellulose ether

- c) at least one water reducing agent selected from sulphonated naphthalene/formaldehyde condensates, sulphonated melamine/formaldehyde condensates, lignosulphonates, modified lignosulphonates, copolymers of linear or cyclic C₄₋₆ olefins and unsaturated ethylenic dicarboxylic acids, (preferably lignosulphonates) and at least one water reducing agent selected from polyhydroxy carboxylic acids and salts thereof and polysaccharides (preferably glucanates).
- d) water
- e) aggregate; and
- f) an anionic surfactant selected from olefin sulphonates and alkyl benzene sulphonates.

Preferably in a mortar according to the invention lime is present.

Yet still further according to the invention there is provided a method for preparing a mortar comprising adding to a mix of hydraulic cement, aggregate and water the following admixture:

- a) a water soluble cellulose ether;
- b) at least one water reducing agent selected from sulphonated naphthalene/formaldehyde condensates, sulphonated melamine/formaldehyde condensates, lignosulphonates, modified lignosulphonates, copolymers of linear or cyclic C₄₋₆ olefins and unsaturated ethylenic dicarboxylic acids, (preferably lignosulphonates) and at least one water reducing agent selected from polyhydroxy carboxylic acid and salts thereof and polysaccharides (preferably glucanates); and
- c) an anionic surfactant selected from olefin sulphonates and alkyl benzene sulphonates.

In a mortar according to the invention the amount of water soluble cellulose ether present is 0.02 to 0.07 % by weight (based on dry weight of cement present).

Preferably in a mortar according to the invention the amount of lignosulphonate present is 0.10 to 0.20 % by weight (based on the dry weight cement present).

Preferably, in a mortar according to the invention the amount of gluconate present is 0.35 to 0.6 % by weight (based on the dry weight of cement).

Preferably in a mortar according to the invention the amount of anionic surfactant is 0.001 to 0.008 % by weight (based on dry weight of cement present).

In a mortar according to the invention the lignosulphonate is preferably sodium lignosulphonate.

In a mortar according to the invention the water soluble cellulose ether is preferably hydroxypropylmethyl cellulose.

In a mortar according to the invention gluconate is preferably sodium gluconate.

In a mortar according to the invention the olefin sulphonate is preferably a sodium alpha olefin sulphonate. More preferably the olefin sulphonate is a C₁₂₋₁₈ olefin sulphonate. By the term α olefin sulphonate is meant a compound having a double bond at the end of the molecule i.e. at the α position and such olefins are usually obtained by cracking a petroleum fraction or by polymerisation of ethylene.

Preferably the amount of lime when present is from greater than 0 to 80 % by weight (based on dry weight of cement present).

Preferably the amount of aggregate present is 200 to 800 % by weight based on the dry weight of cement present.

Preferably the amount of water present is 25 to 65 % by weight based on the dry weight of cement present.

The above described mortars may be premixed mortars which may be delivered and stored at construction sites for as long as 72 hours after the initial mix has been added. The mortars according to the invention have good storage ability and in particular retard the hydration of the mortar during mixing, transport and storage whilst not interfering with the properties needed to utilise the mortar as a cement binding mix. The mortars of the invention remain usable for as long as 72 hours without the need to retemper or extensively remix. The mortars of the invention have excellent adhesive properties to brick or block, adsorption of water from the mix onto the porous surface of building units is uniform, air content is stable and strength needed to support loads placed on it is adequate.

The invention will be illustrated by the following Examples.

Examples 1 to 6

The materials used for these tests were the following:

- (a) Cement: Blend of 3 brands of ordinary portland cement
- (b) Fine Aggregate: Oi River Basin pit sand
- (c) Coarse Aggregate: Ohme crushed stone, max. size = 20 mm
- (d) Flocculating Agent
 - (I) Sodium alginate (hereafter AG-Na)
Five kinds with differing molecular weights were used.
L₂ has a molecular weight of less than 15,000
L has a molecular weight of about 15,000
M has a molecular weight of about 70,000
H has a molecular weight of about 140,000 and
H₂ has a molecular weight of more than 140,000.
 - (II) Sodium carboxymethylcellulose (hereafter CMC) having
a molecular weight of about 20,000
a highly etherized product of low viscosity type was
used; and
- (e) Water-reducing Agents:
 - (I) Sulfonated naphthalene/formaldehyde condensate sodium
salt (hereafter NSF) having a molecular weight of about
2,000.
 - (II) Sulfonated melamine/formaldehyde condensate sodium
salt (hereafter MSF) having a molecular weight of about
2,000.

Mixing of concrete in these tests was done with a 100-liter tilting mixer. The total weight of aggregate used in Examples 1 to 35 is 1900 kg per m³ of total mix.

Examples 1 to 6

The mixture ratios of these examples are given in Table 1 below

A cement mix containing cement, aggregate, a water reducing agent and a flocculating agent (when present) is made up in the proportions given in Table 1 below. The symbols given in the Table are as follows:

W/C is the water to cement ratio ;

S/a is the ratio of fine aggregate to coarse aggregate;

W is the amount of water present ;

C is the amount of cement;

NSF is sulphonated naphthalene/formaldehyde concentrate sodium salt and

AG-Na-M is sodium alginate having a molecular weight of about 70,000

Ex. No.	Dosage (%)		Mix Proportions			
	NSF	AG-Na-M	W/C	S/a (%)	C (kg/m ³)	W (kg/m ³)
1	0.7	0	0.534	47	320	171
2	0.7	0.05	"	"	"	"
3	0.7	0.075	"	"	"	"
4	0.7	0.1	"	"	"	"
5	1.0	0.1	"	"	"	"
6	0.5	0	"	"	"	"

Table 2 shows the slump levels for each of the mixtures of Examples 1 to 6 of Table 1.

TABLE 2

Ex. No.	Upper Level: Slump (cm), Lower Level: Air Content (%)				
	Immediately After	15 Min After	30 Min After	45 Min After	60 Min After
1	Segregated	Segregated	-	-	-
2	21.5 (3.7)	21.5	21.0 (1.6)	19.0	18.0 (2.1)
3	19.0 (4.5)	20.0	18.5 (2.3)	16.0	14.5 (2.4)
4	10.5 (3.3)	12.5	11.5 (2.2)	9.5	7.5 (2.3)
5	20.0 (4.5)	22.5	22.0 (2.5)	22.5	20.5 (2.3)
6	21.0 (2.8)	20.5	16.0 (1.7)	14.5	8.5 (1.9)

Example No. 6 is a mix using NSF alone aiming for a slump of 21 cm immediately after mixing, and this shows a large slump loss. The mix of Example No. 2 is the mix of Example No. 6 to which a high molecular flocculating agent (AG-Na-M) is added with NSF having increased dosage (0.2 percentage) to compensate for reduction in slump immediately after mixing due to addition of the flocculating agent. The cement of this combined use has a slump immediately after mixing of identical level with Example No. 6, but it is seen that subsequent slump loss is minimal. Examples Nos. 3 and 4 are cases where the NSF dosage is constant and the dosage of AG-Na-M is increased. The slump immediately after is smaller with increased dosage of AG-Na-M, but slump loss is also reduced. Example No. 5 is a mix where the dosage of NSF is made larger than Example No. 4. Similarly to Example No. 2, the slump loss was extremely small. Example No. 1 was a mix with AG-Na-M omitted. Segregation occurred and so it was impractical as a concrete mix. In essence, the slump loss reduction effects in Examples Nos. 2 to 5 have been brought about by the combined use of NSF and AG-Na-M, and it is seen that they do not result simply from increase in the dosage of NSF.

Examples 7 to 14

Concrete mixes are made up as in Examples 1 to 6, in which however, the mix proportions are as given in Table 3 and the time-dependent changes in slump in Table 4. The symbols in these Tables are as defined above.

TABLE 3

Test No.	NSP Dosage (%)	AQ-Na		Mix Design			
		Kind	Dosage (%)	W/C	S/a (%)	C (kg/m ³)	W (kg/m ³)
7	1.0	-	-	0.534	47	320	171
8	1.0	L ₂	0.15	"	"	"	"
9	1.0	L	0.10	"	"	"	"
10	1.0	M	0.10	"	"	"	"
11	1.0	H	0.10	"	"	"	"
12	1.0	H	0.05	"	"	"	"
13	1.0	H ₂	0.05	"	"	"	"
14	0.5	-	-	"	"	"	"

TABLE 4

Test No.	Upper Level: Slump (cm), Lower Level: Air Content (%)				
	Immediately After	15 Min After	30 Min After	45 Min After	60 Min After
7	Segregated	Segregated	-	-	-
8	20.5 (5.2)	23.0	22.0 (2.5)	21.5	20.0 (2.5)
9	19.5 (5.0)	22.5	22.0 (2.9)	21.5	20.0 (2.8)
10	19.0 (4.1)	21.5	21.5 (2.2)	21.0	20.5 (2.2)
11	16.0 (4.1)	20.5	19.0 (2.2)	20.0	15.5 (2.2)
12	21.0 (4.5)	23.0	23.0 (2.4)	21.5	21.0 (2.5)
13	19.0 (3.5)	19.5	20.5 (2.1)	21.5	19.0 (2.1)
14	19.5 (3.9)	17.0	11.0 (2.1)	9.0	5.5 (2.0)

It is clear from the above table that the flocculating action becomes greater the larger the molecular weight of AG-Na, and consequently there is a tendency for the slump loss to become smaller after mixture at the same dosage. In other words, there is a tendency for the sufficient dosage to be smaller the larger the molecular weight when slumps immediately after mixing are to be the same. Accordingly, there are appropriate combinations of dosages of NSF and AG-Na when slumps immediately after mixing are to be the same, and it can be seen that this combination varies depending on the molecular weight of AG-Na. Example No. 7 indicates that segregation occurs because of the use of NSF alone.

Examples 15 to 20

Cement mixes are made up similar to those of Examples 1 to 6 having the mix proportions given in Table 5 below. These mixes are superplasticized concrete with the combined addition of NSF and AG-Na-M. By superplasticized concrete is meant a concrete made by adding a superplasticizer (normally a high molecular weight water-reducing agent) to a concrete (called base concrete) consisting of cement, aggregate and water only.

The addition of superplasticizer is generally done after making the base concrete as described above (this is called the delayed addition system), but recently, a system for addition at the time of mixing the base concrete (this is called the simultaneous addition system) has been proposed. Although the simultaneous addition system has the advantage of simplification of the addition procedure, there is economic disadvantage that the dosage of superplasticizer becomes larger than with the delayed addition system, and the situation about slump loss itself still remains unimproved.

The proportions of the mix of concrete are given in Table 5 and the time-dependent changes in slump in Table 6. Superplasticization by the delayed addition system was done 15 minutes after

completion of mixing of base concrete.

TABLE No. 5

Test No.	Super-plasticization System	Base Admixture	Superplasticizer		Mix Design			
			NSP	AQ-Na-M	W/C	S/a (%)	C (kg/m ³)	W- (kg/m ³)
15	Delayed addition	0.25	0.2	-	0.494	47	320	158
16	Delayed addition	0.25	0.3	0.03	"	"	"	"
17	Simultaneous addition	0.25	0.5	-	"	"	"	"
18	Simultaneous addition	0.25	0.75	0.05	"	"	"	"
19	Simultaneous addition	-	1.0	0.05	"	"	"	"
20	Simultaneous addition	-	1.5	0.075	"	"	"	"

Note: 1) By base admixture is meant the admixture used when making the base concrete, which in this case was a commercial air-entraining water-reducing agent, Pozzolith 70 (P-70). This is present in the base concrete.

2) The figures in the columns for "Base Admixture" and "Superplasticizer" indicate the respective dosages (%) based on the dry weight of cement present.

TABLE No. 6

Test No.	Upper Level: Slump (cm), Lower Level: Air Content (%)					
	Before Superplasticization	Immediately After Superplasticization	15 Min After	30 Min After	45 Min After	60 Min After
15	8.0 (4.4)	18.0 (2.6)	13.5	10.0 (1.8)	8.5	7.5 (1.7)
16	8.0 (4.5)	18.5 (3.9)	19.0	19.0 (2.8)	18.0	17.5 (2.9)
17	-	18.5 (4.6)	14.5	11.0 (2.3)	8.5	7.5 (2.5)
18	-	19.0 (4.3)	20.0	20.0 (2.7)	19.5	19.5 (2.7)
19	-	21.0 (4.5)	23.0	23.0 (2.4)	21.5	21.0 (2.5)
20	-	18.0 (4.7)	21.0	22.5 (3.2)	22.5	22.5 (3.1)

Note: By "Immediately After Superplasticization" in Examples Nos. 15 to 20 is meant "immediately after discharge after completion of mixing in mixer."

Examples Nos. 15 and 17 indicate cases of conventional delayed addition and simultaneous addition systems using NSF as the superplasticizer, and slump losses after superplasticization are large in both cases.

As is clear from Examples Nos. 16 and 18 the method of this invention is effectively applied to either the delayed addition system or the simultaneous addition system for superplasticized concrete.

Examples Nos. 19 and 20 are cases to confirm that the combined use of AG-Na-M irrespective of the fact that there is a large amount of superplasticizer (NSF) present produces favourable results.

Examples 21 to 24

In a similar fashion to the Examples 15 to 20 cement mixtures are made up having the proportions given in Table 7 below and the time-dependent changes in slump are given in Table 8.

TABLE No. 7

Test No.	NSF Dosage (%)	CMC Dosage (%)	Mix Design			
			W/C	S/a (%)	C (kg/m ³)	W (kg/m ³)
21	0.7	0.10	0.534	47	320	171
22	0.7	0.20	"	"	"	"
23	0.7	0.30	"	"	"	"
24	0.5	-	"	"	"	"

TABLE No. 8

Test No.	Upper Level: Slump (cm), Lower Level: Air Content (%)				
	Immediately After	15 Min After	30 Min After	45 Min After	60 Min After
21	21.5 (4.0)	22.0	20.5 (2.1)	19.5	17.0 (2.3)
22	20.0 (3.7)	19.5	20.0 (1.8)	20.0	18.0 (1.5)
23	18.5 (4.5)	20.0	19.0 (2.3)	19.5	17.5 (2.3)
24	20.0 (3.0)	17.5	14.0 (2.1)	12.5	8.0 (2.0)

Examples Nos. 21 to 23 are mixes having the amount of NSF dosage increased by 0.2 percentage points over the mix of No. 24 with CMC dosages being 0.1 to 0.3 percent, and it can be seen that the situation regarding slump loss is greatly improved by the combined addition. Examples 21 to 23 are mixes having a constant NSF dosage with CMC dosage gradually increased, and it can be seen that slump immediately after mixing and slump loss is gradually reduced because of increased flocculating action due to increase in CMC dosage. However, this tendency is less than with AG-Na.

Examples 25 to 31

Cement mixes similar to those of Examples 1 to 6 are made up of superplasticized concrete in case of using CMC as the high molecular flocculating agent. The mix proportions are given in Table No. 9 below, and time-dependent changes in slump in Table 10.

Comparisons are shown between delayed and simultaneous additions of the NSF and CMC to the base mix.

TABLE No. 9

Test No.	Super-plasticization System	Base Admixture	Superplasticizer		Mix Design			
			NSP	CMC	W/C	S/a (%)	C (kg/m ³)	W (kg/m ³)
25	Delayed addition	0.25	0.2	-	0.494	47	320	158
26	Delayed addition	0.25	0.3	0.1	"	"	"	"
27	Delayed addition	0.25	0.25	0.1	"	"	"	"
28	Simultaneous addition	0.25	0.50	-	"	"	"	"
29	Simultaneous addition	0.25	0.75	0.3	"	"	"	"
30	Simultaneous addition	-	0.75	0.2	"	"	"	"
31	Simultaneous addition	-	1.0	0.3	"	"	"	"

TABLE No. 10

Test No.	Upper Level: Slump (cm), Lower Level: Air Content (%)					
	Before Superplasticization	Immediately After Superplasticization	15 Min After	30 Min After	45 Min After	60 Min After
25	8.5 (4.4)	18.0 (2.6)	13.5	10.0 (1.7)	8.5	7.5 (1.7)
26	8.5 (4.4)	19.0 (3.9)	20.0	19.5 (2.8)	17.5	17.0 (2.9)
27	8.5 (4.4)	18.0 (4.0)	19.0	19.0 (3.5)	17.0	16.0 (3.0)
28	-	18.5 (4.4)	14.5	11.0 (2.3)	9.0	7.5 (2.0)
29	-	18.5 (4.1)	19.5	19.5 (2.5)	19.0	18.0 (2.6)
30	-	19.5 (4.7)	20.5	20.5 (2.1)	20.0	18.5 (2.3)
31	-	17.5 (4.9)	22.5	21.0 (2.5)	21.0	20.5 (2.4)

As is clear from the above table, it can be seen that when CMC is used as the high molecular flocculating agent, it is also effective for application of the method of this invention to superplasticized concrete.

Examples 32 to 35

Cement mixes similar to those of Examples 1 to 6 have been up using MSF as the water-reducing agent and CMC as the high molecular weight flocculating agent. The mix proportions are given in Table No. 11 and the time-dependent changes in slumps in Table 12.

TABLE No. 11

Test No.	Dosage (%)		Mix Design			
	MSP	CMC	W/C	S/a (%)	C (kg/m ³)	W (kg/m ³)
32	1.0	-	0.534	47	320	171
33	1.0	0.2	"	"	"	"
34	1.4	0.35	"	"	"	"
35	1.7	-	"	"	"	"

TABLE No. 12

Test No.	Upper Level: Slump (cm), Lower Level: Air Content (%)				
	Immediately After	15 Min After	30 Min After	45 Min After	60 Min After
32	Segregated	Segregated	-	-	-
33	20.0 (3.8)	20.0	19.5 (2.2)	19.5	19.0 (2.1)
34	21.0 (4.3)	21.5	21.0 (2.5)	20.0	19.0 (2.6)
35	20.0 (3.0)	17.5	15.0 (2.1)	12.5	8.0 (2.0)

Example 35 is a concrete mix using MSF such that the initial slump is 20 cm. The slump loss of this concrete was large. Examples Nos. 33 and 34 are mixes with combined addition of MSF and CMC and slump losses were small. Example No. 32 is a mix only using MSF and in which segregation occurs.

All mortar proportions by volume for Examples No.s 36 to 40 are determined in accordance with ASTM Designation C 270-80-Standard Specification to Mortar for Unit Masonry Mortar Types (= Table 2).

Examples 36 to 38

A mortar mix is made up containing 898 g of Type 1 Portland cement, 100 g of masonry lime, 2840 g of masonry sand with a measured fineness modulus of 1.81 in half the required water for each example in a paddle type Hobart mixer.

An admixture comprising 0.52 % sodium gluconate, 0.175 % sodium lignosulphonate, 0.07 % hydroxypropylmethylcellulose and 0.008 % α -olefin sulphonate (all percentages are based on dry cement present in the combined mortar mix) is made up. The admixture is added to the mortar mix and additional water is added until the desired workability is achieved. The total amount of water present is about 540 g. The hydroxy propylmethyl cellulose has a molecular weight of about 120,000.

The water to cement ratios are used as given in Table 13 below.

TABLE No. 13

	<u>Ex. 36</u>	<u>Ex. 37</u>	<u>Ex. 38</u>
Water: cement ratio	0.59	0.50	0.55
Air content % (by volume (1))	24.00	21.70	17.70
Flow % (2)	125	98	115
Cone penetration (3)	68	58	43
Adhesion (brick)	good	good	good
Adhesion (block)	good	good	good
Scratch resistance	good	good	good
Workability	good	good	good
cohesiveness	good	good	good
Consistency (48 hours after mixing)	pliable	pliable	pliable

The lignosulphonate used has a molecular weight of 2,000

- (1) ASTM Designation C 185-80 Standard Test Method for Air Content of Hydraulic Cement Mortar.
- (2) ASTM Designation C 102-00 Standard Test Method for Compressive Strength of Hydraulic Cement Mortars.
- (3) ASTM Designation: C 472-79 Standard Methods for Physical Testing of Gypsum Plasters and Gypsum Concrete.

Examples 39 and 40

These examples comprise a mortar mix containing approximately 0.3 % water (based on the dry weight of cement), 898 g of Type 1 Portland Cement, 100 g of masonry lime and 2840 g of masonry sand with a measured fineness of 1.81 in half the required water in a paddle type Hobart mixer. The appropriate admixture for Examples 39 and 40 given in Table 13 below, is then added.

TABLE 14

	Amount of Lignosulphonate	Amount of sodium gluconate
Example 39	—	0.52 %
40	0.175 %	—

all % are based on the amount of cement present.

The properties of these mixes are given in Table 15 below

TABLE 15

	Example 39	Example 40
Water: cement ratio	0.59	0.59
Air content % by volume	7.40	8.20
Flow %	114	103
Cone penetration	30	36
Adhesion (Brick)	Poor	None
Adhesion (Block)	Poor	None
Scratch Resistance	Fair	Good
Workability	Poor	Poor
Cohesiveness	Poor	None
Consistency 48 hours after mixing	Dry	Hard

Examples 41 to 47

Cement mixes were made up analogously to the method of Examples 1 to 6 using lignosulphonate instead of NSF as the water reducing agent.

In these Examples the materials used were the following:

- a) Cement: A mix of 3 brands of Normal Portland Cement from Onoda, Asano and Sumitomo in equal quantities.
- b) Fine aggregate: Oi River Basin pit sand
- c) Coarse aggregate: Ohme crushed stone.
- d) Lignosulphonate: (LIG) George Pacific's LIG having a molecular weight of about 2,000.
- e) Flocculating agent: CMC with a molecular weight of about 20,000.
- f) Air entraining water reducing agent: Pozzolith 70

The amount of concrete made is 80 liters and the air temperature is 20°C. Air entraining agent is initially added in such an amount that the air content is about 5 %. The mixes and results for simultaneous addition are given in Table 16 and for delayed addition are given in Table 17.

TABLE No. 16 - Simultaneous Addition

EX. No.	W/C (%)	S/a (%)	Unit Qty.		(kg/cm)	Admixture		Slump-upper level Air content-lower level Elapse of time (min.)					
			C	W		Type	Dosage	0	15	30	45	60	
41	60	49	320	192		Plain	--	18.5	18.5	16.5	16.5	15.5	15.5
								1.8		1.5		1.6	
42	54	47	320	173		P-70	250ml/ 100kg	19.0	17.0	16.5	14.5	13.5	13.5
								4.8		3.1		3.7	
						LIG	0.35%	19,0	18.5	18.0	18.5	18.0	18.0
43	54	47	320	173		CMC	0.15%	5.5		4.8		4.3	

3700/DH/AB

Table No. 17 - Delayed Addition

EX. No.	W/C (%)	S/a (%)	Unit Qty. (kg/cm)		Admixture		Slump-upper level Air content-lower level Elapse of time (min.)					
							Before Delayed * Addition	0	15	30	45	60
44	60.0	49	320	192	Plain	—	—	18.5	18.5	16.5	16.5	15.5
							—	1.8		1.5		1.6
45	50.6	47	320	162	LIG	0.18%	8.0	20.0	20.0	19.5	17.5	15.0
							4.1	4.8		3.9		4.3
46	50.6	47	320	162	LIG	0.25	9.0	18.5	23.0	21.5	21.5	19.5
					CMC	0.1	4.1	5.5		3.8		3.6
47	50.6	47	320	162	LIG	0.22	9.0	18.5	20.0	19.5	20.5	17.5
					CMC	0.08	4.1	3.9		3.2		3.2

CLAIMS

1. A cement mix comprising

- a) hydraulic cement;
- b) one or more flocculating agents, selected from sodium alginate, water soluble cellulose ether, polyacrylates, polyacrylamides, guar gum, gelatin, chitosan, dextrin and dialdehyde starches;
- c) one or more water reducing agents selected from sulphonated naphthalene/formaldehyde condensates, sulphonated melamine/formaldehyde condensates; lignosulphonates, modified lignosulphonates, salts of polyhydroxy carboxylic acids, polyhydroxy carboxylic acids, glucosaccharides, copolymers of linear or cyclic C₄₋₆-olefins and unsaturated ethylenic dicarboxylic acids;
- d) aggregate; and
- e) water.

2. A mix according to Claim 1 in which the flocculating agents are selected from water soluble cellulose ethers and sodium alginate.

3. A mix according to Claims 1 or 2 in which the water reducing agents are selected from sulphonated naphthalene/formaldehyde condensates, sulphonated melamine/formaldehyde condensates, sodium lignosulphonates and alkali-treated or ultra-filtered modified lignosulphonates.

4. A mix according to any one of the preceding claims in which the amount of flocculating agent present is 0.01 to 0.5 % by weight (based on the dry weight of cement present).

5. A mix according to any one of the preceding claims in which the amount of water reducing agent present is 0.10 to 1.0 % by weight (based on the dry weight of cement present).

6. A method for fluidizing a cement mix including aggregate and water comprising adding one or more high molecular weight flocculating agents selected from sodium alginate, a water soluble cellulose ether, polyacrylates, polyacrylamides, guar gum, gelatin, chitosan, dextrin and dialdehyde starches and one or more water reducing agents selected from sulphonated naphthalene/formaldehyde condensates, sulphonated melamine/formaldehyde condensates, lignosulphonates, modified lignosulphonates, salts of polyhydroxy carboxylic acids, polyhydroxy carboxylic acids, glucosaccharides, copolymers of linear and cyclic C₄₋₆olefins and unsaturated ethylenic dicarboxylic acids to the cement mix.

7. A mortar comprising:

- a) a hydraulic cement
- b) a water soluble cellulose ether
- c) at least one water reducing agent selected from sulphonated naphthalene/formaldehyde condensates, sulphonated melamine/formaldehyde condensates, lignosulphonates, modified lignosulphonates, copolymers of linear or cyclic C₄₋₆ olefins or unsaturated ethylenic dicarboxylic acids, and at least one water reducing agent selected from polyhydroxy carboxylic acid and salts thereof and polysaccharides
- d) water
- e) aggregate and
- f) an anionic surfactant selected from olefin sulphonates and alkylbenzene sulphonates.

8. A mortar according to Claim 7, in which component c comprises at least a lignosulphonate and a gluconate.

9. A mortar according to Claim 7 or Claim 8 in which the amount of water-soluble cellulose ether present is 0.02 to 0.07 % by weight (based on dry weight of cement present).

10. A mortar according to Claims 8 or 9 in which the amount of lignosulphonate present is 0.10 to 0.20 % by weight (based on the dry weight cement present).

11. A mortar according to anyone of Claims 8 to 10 in which the amount of gluconate present is 0.35 to 0.6 % by weight (based on dry weight of cement).

12. A mortar according to any one of Claims 7 to 11, in which the amount of anionic surfactant is 0.001 to 0.008 % by weight (based on dry weight of cement present).

13. A method for preparing a mortar according to any one of Claims 7 to 12 comprising adding to a mix of hydraulic cement, aggregate and water the following admixture:

- a) a water-soluble cellulose ether;
- b) at least one water reducing agent selected from sulphonated naphthalene/formaldehyde condensates, sulphonated melamine/formaldehyde condensates, lignosulphonates, modified lignosulphonates, copolymers of linear or cyclic C₄₋₆ olefins and unsaturated ethylenic dicarboxylic acids, and at least one water reducing agent selected from polyhydroxy carboxylic acids and salts thereof and polysaccharides;
and
- c) an anionic surfactant selected from olefin sulphonates or alkyl benzene sulphonates.

14. A method for preparing a mortar comprising adding to a mix of hydraulic cement, aggregate and water the following admixture:

- a) 0.02 to 0.07 % by weight (based on the dry weight of cement present) of a water-soluble cellulose ether;
- b) 0.10 to 0.20 % by weight (based on the dry weight of cement present) of a lignosulphonate and 0.35 to 0.575 % by weight (based on dry weight of cement present) of a gluconate; and
- c) 0.001 to 0.008 % by weight (based on the dry weight of cement present) of an olefin sulphonate.

AMENDED CLAIMS

[received by the international Bureau on 27 December 1985 (27.12.85);
original claims 1-14 replaced by new claims 1-10 (2 pages)]

1. A cement mix comprising
 - a) hydraulic cement
 - b) hydroxypropyl methylcellulose
 - c) a lignosulphonate or modified lignosulphonate
 - d) aggregate and
 - e) water.
2. A cement mix according to Claim 1 in which d) is fine aggregate and lime is additionally present.
3. A cement mix according to Claim 1 or Claim 2 containing additionally a compound selected from polyhydroxycarboxylic acids and salts thereof and polysaccharides.
4. A cement mix according to Claim 3 in which the additional component is a gluconate.
5. A mortar comprising
 - a) a hydraulic cement
 - b) hydroxypropyl methylcellulose
 - c) a lignosulphonate or modified lignosulphonate and at least one compound selected from polyhydroxycarboxylic acids and salts thereof and polysaccharides.
 - d) aggregate
 - e) water
 - and f) an anionic surfactant selected from olefin sulphonates and alkylbenzene sulphonates.
6. A mortar comprising
 - a) a hydraulic cement
 - b) hydroxypropyl methylcellulose
 - c) sodium or calcium lignosulphonate and sodium gluconate
 - d) aggregate
 - e) water
 - and f) a sodium alpha olefin sulphonate.

7. A mortar according to Claim 6 in which the amount of component b) is 0.02 to 0.07 %, of lignosulphonate is 0.10 to 0.20%, of sodium gluconate is 0.35 to 0.6%, of component d) is 200-800%, of component e) is 25-65% and of component f) is 0.001 to 0.008%, all percentages being by weight based on the dry weight of cement present.

8. A mortar according to any one of Claims 5 to 7 containing in addition up to 80% of lime by weight based on the dry weight of cement present.

9. A method for preparing a mortar according to Claim 5 comprising adding to a mix of hydraulic cement, aggregate and water the following admixture

- a) hydroxypropyl methylcellulose
- b) a lignosulphonate or modified lignosulphonate and at least one compound selected from polyhydroxy carboxylic acids and salts thereof and polysaccharides and
- c) an anionic surfactant selected from olefin sulphonates and alkylbenzene sulphonates.

10. A method according to Claim 9 comprising adding to a mix of hydraulic cement aggregate and water the following admixture:

- a) 0.02 to 0.07% of hydroxypropyl methylcellulose
- b) 0.10 to 0.20% of sodium or calcium lignosulphonate and 0.35 to 0.6% of sodium gluconate and
- c) 0.001 to 0.008% of sodium alpha olefin sulphonate,

all percentages being by weight based on the dry weight of cement present.

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 85/00294

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) * According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁴ : C 04 B 28/02 // (C 04 B 28/02, 24:06, 24:14, 24:16, 24:26, 24:38)																													
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 30%; border-bottom: 1px solid black;">Classification System¹</td> <td style="border-bottom: 1px solid black;">Classification Symbols</td> </tr> <tr> <td style="padding: 5px;">IPC⁴ C 04 B 28/00</td> <td></td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched⁸</div>			Classification System ¹	Classification Symbols	IPC ⁴ C 04 B 28/00																								
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III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category⁶</th> <th style="width: 70%; border-bottom: 1px solid black;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 20%; border-bottom: 1px solid black;">Relevant to Claim No.¹³</th> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;">GB, A, 2114985 (W.C. GRACE) 1 September 1983, see page 1, lines 4-7, 37-43, 51-52; claims 1 and 7 --</td> <td style="text-align: center; vertical-align: top;">1, 3-6</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;">FR, A, 1502387 (MO OCH DOMSJO) 18 November 1967, see abstract 1° --</td> <td style="text-align: center; vertical-align: top;">1, 2, 4, 6</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;">FR, A, 1543999 (CH. LALEMAN) 31 October 1968 --</td> <td style="text-align: center; vertical-align: top;">1-6</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;">FR, A, 2154035 (SUDDEUTSCHE KALKSTICKSTOFFWERKE) 4 May 1973, see claim 1; page 2, lines 1-5 --</td> <td style="text-align: center; vertical-align: top;">1-4, 6</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td style="vertical-align: top;">FR, A, 2085402 (PLASTIC FIN) 24 December 1971, see page 3, lines 5-13; formule II --</td> <td style="text-align: center; vertical-align: top;">1-3, 6-9, 13</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td style="vertical-align: top;">FR, A, 2114734 (KALLE AG) 30 June 1972, see claims 1 and 6 --</td> <td style="text-align: center; vertical-align: top;">1-3, 6-9, 13</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td style="vertical-align: top;">GB, A, 2040907 (KAD SOAP) 3 September 1980, see abstract --</td> <td style="text-align: center; vertical-align: top;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td style="vertical-align: top;">GB, A, 2083015 (WILHELM SCHON K.G.) 17 March 1982, see claims 1, 13; page 2, lines --</td> <td style="text-align: center; vertical-align: top;">7, 8</td> </tr> </table>			Category ⁶	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	GB, A, 2114985 (W.C. GRACE) 1 September 1983, see page 1, lines 4-7, 37-43, 51-52; claims 1 and 7 --	1, 3-6	X	FR, A, 1502387 (MO OCH DOMSJO) 18 November 1967, see abstract 1° --	1, 2, 4, 6	X	FR, A, 1543999 (CH. LALEMAN) 31 October 1968 --	1-6	X	FR, A, 2154035 (SUDDEUTSCHE KALKSTICKSTOFFWERKE) 4 May 1973, see claim 1; page 2, lines 1-5 --	1-4, 6	Y	FR, A, 2085402 (PLASTIC FIN) 24 December 1971, see page 3, lines 5-13; formule II --	1-3, 6-9, 13	Y	FR, A, 2114734 (KALLE AG) 30 June 1972, see claims 1 and 6 --	1-3, 6-9, 13	A	GB, A, 2040907 (KAD SOAP) 3 September 1980, see abstract --	1	A	GB, A, 2083015 (WILHELM SCHON K.G.) 17 March 1982, see claims 1, 13; page 2, lines --	7, 8
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<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; vertical-align: top;"> <p>* Special categories of cited documents:¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </td> <td style="width: 50%; vertical-align: top;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Δ" document member of the same patent family</p> </td> </tr> </table>			<p>* Special categories of cited documents:¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Δ" document member of the same patent family</p>																									
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IV. CERTIFICATION																													
Date of the Actual Completion of the International Search <div style="text-align: center; font-weight: bold;">3rd October 1985</div>	Date of Mailing of this International Search Report <div style="text-align: center; font-weight: bold;">06 NOV. 1985</div>																												
International Searching Authority <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: right;"> G.L.M. Knudsenberg </div>																												

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
	89-96,118-130 --	
A	Kirk-Othmer "Encycl. of Chem. Technology", 3rd Edition, volume 10 J. Wiley & Sons, New York, pages 496-512, see pages 509-512 -----	

INTERNATIONAL APPLICATION NO. PCT/EP 85/00294 (SA 9927)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 29/10/85

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 2114985	01/09/83	SE-A- 8206104	27/10/82
		FR-A- 2521549	19/08/83
		DE-A- 3305098	18/08/83
		JP-A- 58145651	30/08/83
		AU-A- 9037482	25/08/83
		US-A- 4460720	17/07/84
FR-A- 1502387		None	
FR-A- 1543999		None	
FR-A- 2154035	04/05/73	NL-A- 7210934	20/03/73
		DE-A, B 2146709	22/03/73
		GB-A- 1340159	12/12/73
		CH-A- 564492	31/07/75
FR-A- 2085402	24/12/71	None	
FR-A- 2114734	30/06/72	NL-A- 7115273	18/05/72
		DE-A, B, C 2056255	25/05/72
		AT-B- 319126	10/12/74
		US-A- 3926650	16/12/75
		CA-A- 980369	23/12/75
		CH-A- 577945	30/07/76
		DE-A, C 2150395	12/04/73
GB-A- 2040907	03/09/80	FR-A, B 2446803	14/08/80
		DE-A- 3000245	31/07/80
		JP-A- 55095656	21/07/80
		CA-A- 1128698	27/07/82
GB-A- 2083015	17/03/82	LU-A- 83510	01/12/81
		BE-A- 889755	16/11/81
		FR-A, B 2487330	29/01/82
		DE-A, C 3028559	11/02/82
		NL-A- 8103518	16/02/82
		CH-B- 650759	15/08/85

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